

Excess Vibrational Modes and the Boson Peak in Model Glasses

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(Dated: February 6, 2008)

The excess low-frequency normal modes for two widely-used models of glasses were studied at zero temperature. The onset frequencies for the anomalous modes for both systems agree well with predictions of a variational argument, which is based on analyzing the vibrational energy originating from the excess contacts per particle over the minimum number needed for mechanical stability. Even though both glasses studied have a high coordination number, most of the additional contacts can be considered to be weak.

PACS numbers: 61.43.Fs, 64.70.Pf, 83.80.Fg

Our understanding of liquids is based on the idea that liquid structure is largely determined by strong short-ranged repulsions and that the longer-ranged attractions can be treated as a perturbation [1]. Similar considerations were used to study jamming at zero temperature as a function of density ϕ [2, 3]. When only finite-ranged repulsions are included, so that non-overlapping particles do not interact, there is a sharp jamming transition at ϕ_c . In such systems, the low-frequency normal modes of vibration in the marginally jammed state are fundamentally different from the long-wavelength plane waves expected from elasticity theory [2, 3]. The unusual nature of the modes is reflected in the density of vibrational states, $D(\omega)$, versus frequency, ω [2, 3]. At the transition, $D(\omega)$ has a plateau extending to $\omega = 0$. This is very different from the expected Debye scaling $D(\omega) \propto \omega^{d-1}$ in d dimensions [4], which is normally observed in solids. At densities above ϕ_c , the plateau no longer extends to $\omega = 0$ but terminates at a frequency ω^* . The dramatic rise in $D(\omega)$ at ω^* corresponds to the onset of anomalous modes. Similar excess modes, whose origins are still debated [5, 6, 7, 8, 9, 10, 11, 12], are observed in glasses. The anomalous modes in glasses give rise to what is known as the boson peak [13, 14, 15, 16], and are believed to be responsible for many characteristic low-temperature phenomena [17].

In this paper, we demonstrate that the theoretical framework [18, 19, 20] used to explain the modes in marginally jammed solids at zero temperature can be extended to the anomalous modes in two more realistic models of “repulsive glasses,” by which we mean systems that undergo glass transitions due to the repulsive part of their potentials as the temperature is lowered. The zero-temperature jamming transition of spheres with finite-ranged repulsions, which we will call Point J to distinguish from other jamming transitions, coincides with the density at which the system has just enough contacts to satisfy the constraints of mechanical equilibrium [2]. This is called the isostatic condition. The average coordination number z (*i.e.* the average number of particles with which a given particle interacts) needed for mechanical stability is $z_c = 2d$, where d is the spatial dimension

[21, 22]. By compressing the system or increasing the range of interaction, we increase z . These extra contacts suppress anomalous modes at low frequencies [18, 19, 20]. We will show that in systems with long-ranged interactions, there is a well-defined division between a relatively few strong repulsive interactions (stiff contacts) and the more numerous weaker interactions (including attractions), which can be treated as a correction.

We will study the onset frequency of the anomalous modes, ω^\dagger , in two widely-used models of glasses and the glass transition and compare the simulation results with theoretical predictions [20]. We use a mixture of 800 A and 200 B spheres with equal mass m interacting in three dimensions via the Lennard-Jones potential [23]:

$$V(r_{ij}) = \frac{\epsilon_{ij}}{72} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right], \quad (1)$$

where r_{ij} is the separation between particles i and j and ϵ_{ij} and σ_{ij} depend on the type of particles under consideration: $\epsilon_{AB} = 1.5\epsilon_{AA}$, $\epsilon_{BB} = 0.5\epsilon_{AA}$ and $\sigma_{AB} = 0.8\sigma_{AA}$, and $\sigma_{BB} = 0.88\sigma_{AA}$. The potential is cut off at $r_{ij} = 2.5\sigma_{ij}$ and shifted to satisfy $V(2.5\sigma_{ij}) = V'(2.5\sigma_{ij}) = 0$. For these systems, the density is given in units of $\rho = N\sigma_{AA}^3/L^3$ and ϵ_{AA} , σ_{AA} and m are set to unity. We restrict the densities to lie above $\rho \approx 1.2$, where the pressure is positive. When this is not the case, there can be low-frequency modes arising from rather different physics [22].

For comparison we also study a system with purely repulsive interactions where ϕ_c exists. We simulate a mixture of 500 A and 500 B spheres with $\sigma_B = 1.4\sigma_A$ and equal mass m , interacting via the repulsive Lennard-Jones potential [1]

$$V(r_{ij}) = \begin{cases} \frac{\epsilon}{72} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - 2 \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 + 1 \right], & r_{ij} < \sigma_{ij}, \\ 0, & r_{ij} \geq \sigma_{ij}, \end{cases} \quad (2)$$

where ϵ is the characteristic energy, and $\sigma_{ij} = (\sigma_i + \sigma_j)/2$. For these systems, we characterize density with the packing fraction $\phi = \pi/6(N_A\sigma_A^3 + N_B\sigma_B^3)/L^3$. We set $\epsilon = 1$,

$m = 1$, and $\sigma_A = 1$. The simulations were all carried out in a cubic box with periodic boundary conditions. We study zero-temperature ($T = 0$) configurations which were obtained by quenching initially random ($T = \infty$) configurations of particles to their local energy minima at $T = 0$ using conjugate gradient energy minimization [24].

In the harmonic expansion, the energy of particle displacements $\delta\vec{R}_i$ from their equilibrium positions is:

$$\delta E = \frac{1}{2} \sum_{i,j} \left[V''(r_{ij})(\delta\vec{R}_{ij} \cdot \hat{r}_{ij})^2 + \frac{V'(r_{ij})}{r_{ij}} (\delta\vec{R}_{ij}^\perp)^2 \right] \quad (3)$$

where V' and V'' are the first and second derivatives of the pair potential $V(r)$ with respect to r , and $\vec{r}_{ij} = r_{ij}\hat{r}_{ij}$ is the equilibrium separation vector between particles i and j . Here, $\delta\vec{R}_{ij} \equiv \delta\vec{R}_i - \delta\vec{R}_j$, and $\delta\vec{R}_{ij}^\perp$ is the projection of $\delta\vec{R}_{ij}$ on the plane perpendicular to \hat{r}_{ij} . We diagonalize the dynamical matrix [4] to obtain normal modes $|n\rangle$, and their corresponding eigenvalues \mathcal{E}_n . The normal-mode frequencies are $\omega_n^2 = \mathcal{E}_n$, where the index n runs from 1 to Nd . From these frequencies, we calculate the density of vibrational states per particle, $D(\omega)$. It is instructive to also calculate $D^{(0)}(\omega)$, obtained by neglecting the second term in Eq. 3 (*i. e.* the stress term). This corresponds to replacing $V(r)$ with unstretched springs, each chosen to have the same stiffness $V''(r)$ as for the original potential.

In Fig. 1(a) and (b), we show two curves, $D(\omega)$ (heavy curves) and $D^{(0)}(\omega)$ (light curves), corresponding to the stressed and unstressed cases, at each density. Fig. 1(a) shows results for the repulsive Lennard-Jones systems. Close to the unjamming transition, these systems are approximately equivalent to the repulsive harmonic systems studied previously [2, 3]. Just above the transition, $D(\omega)$ has a plateau down to $\omega = 0$. Upon compression the onset of these anomalous modes shifts up to ω^* , below which $D(\omega)$ decreases to zero. Fig. 1(b) shows the results for the system with Lennard-Jones interactions. Because there are attractive interactions, the jamming transition lies inside the liquid-vapor spinodal [2, 25] and is inaccessible. Thus, the plateau in the density of states never extends to $\omega = 0$.

It is important to note that $D^{(0)}(\omega)$ falls much more sharply than $D(\omega)$ as ω decreases below ω^* , but that $D(\omega)$ and $D^{(0)}(\omega)$ are nearly indistinguishable above ω^* . Here, ω^* corresponds to the onset of the anomalous modes in unstressed systems. At high densities, the sharp peaks in $D^{(0)}(\omega)$ below ω^* arise from linear combinations of nearly-degenerate long-wavelength plane waves. (The lowest peak has plane waves with wavevector, $k_1 = 2\pi/L$ where L is the box size, while the second peak has $k_2 = 2\sqrt{2}\pi/L$ as one would expect for the two lowest frequency modes in an elastic solid.) Thus, the onset of anomalous modes lies above these peaks. In the infinite system-size limit, the peaks should smooth out to yield the normal scaling: $D(\omega) \sim \omega^{d-1}$ in d dimensions.

We now recapitulate the theoretical ideas that address the properties of high-coordination systems [20]. In gen-

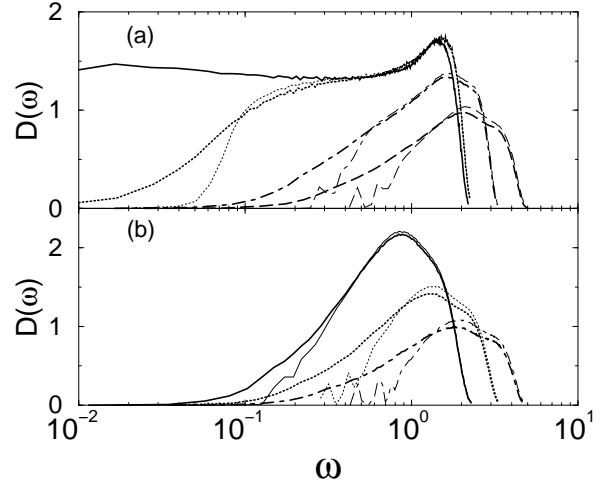


FIG. 1: Density of vibrational states per particle of 3D glasses of $N = 1000$ particles. We plot $D(\omega)$ for stressed systems (heavy curves) and $D^{(0)}(\omega)$ for unstressed systems (light curves) interacting via (a) the repulsive Lennard-Jones potential at $\Delta\phi = 10^{-6}$ (solid), 10^{-2} (dotted), 0.1 (dot-dashed), and 0.2 (dashed); and (b) the Lennard-Jones potential at $\rho = 1.2$ (solid), 1.4 (dotted) and 1.6 (dashed).

eral, extra contacts increase the frequency of the lowest-frequency anomalous modes in two ways: (i) they can increase the energy cost of a mode by adding extra nodes so that some bonds are unstretched during an oscillation, and (ii) they can leave the number of nodes fixed but instead increase the average restoring force (and therefore the energy) for the normal-mode displacement.

A variational argument calculates an upper bound for the energy of a normal mode by minimizing the energy with respect to these two contributions. The first term in Eq. 3 indicates that a good trial function would have nodes, *i. e.*, small values of $(\delta\vec{R}_{ij} \cdot \hat{r}_{ij})^2$, where V'' is large. Thus the $z_1 N/2$ contacts with the highest values of V'' introduce nodes in the trial function. The remaining $(z - z_1)N/2$ contacts increase the energy of the trial mode by increasing the restoring force for displacements according to the first term in Eq. 3 [20]. We rewrite Eq. 3 as

$$\begin{aligned} \delta E^{(0)} &= \delta E_1 + \delta E_2, \\ \delta E &= \delta E^{(0)} + \delta E_3, \end{aligned} \quad (4)$$

where δE_1 , δE_2 and δE_3 represent the energy costs associated respectively with the $z_1 N/2$ stiffest contacts, the remaining $(z - z_1)N/2$ weak contacts, and the contribution of the stress term (the second term in Eq. 3; see Ref. [19]). Note that $\delta E^{(0)}$ is the energy cost of a mode for the unstressed system.

We now construct approximate expressions for these contributions. Ref. [18] argues that $\delta E_1 \approx A_1 k_1 (z_1 - z_c)^2$, where $k_1 = \langle V'' \rangle_1$ is the average over the $z_1 N/2$ contacts with the highest values of V'' . This is consistent with earlier simulation results for harmonic springs for $z_1 -$

$z_c \leq 3$ [19]. While k_1 varies strongly with density and potential, we expect A_1 to depend only weakly on these quantities [26]. To obtain A_1 , we compare to simulations of unstressed systems with springs of equal stiffness. The precise value of A_1 depends on which point in the density of states we choose to represent the onset of anomalous modes. In the following analysis, we use the value ω^\dagger where $D^{(0)}(\omega)$ reaches 0.25 of its maximum height, which fixes $A_1 = 0.018$. We would have obtained a somewhat different constant if we had compared with data at a different point in the rise, but the difference would be small because $D^{(0)}(\omega)$ rises abruptly.

To estimate δE_2 , we assume that for the normalized trial mode, the displacements of i and j are uncorrelated with each other if i and j are connected by weak contacts. Then $\langle (\delta \vec{R}_{ij} \cdot \hat{r}_{ij})^2 \rangle \approx 2/Nd$ for an N -particle system in d dimensions [20]. Thus $\delta E_2 \approx \frac{1}{Nd} \sum_{ij}^w V''(r_{ij})$, where the sum \sum^w runs only over pairs of particles i and j connected by the $(z - z_1)N/2$ weakest contacts. We have shown numerically that this approximation is reasonable for a system with particles connected by harmonic springs at their equilibrium lengths with two very different stiffnesses. For such a system, the stiff springs contribute only to δE_1 , the weak springs contribute only to δE_2 . Our expressions for δE_2 and δE_1 were thus verified cleanly.

We estimate δE_3 as follows. For uncorrelated displacements between particles i and j , $\langle (\delta \vec{R}_{ij}^\perp)^2 \rangle \approx 2(d-1)/dN$, leading to $\delta E_3 = A_3 \mathcal{S}$, where $\mathcal{S} \equiv 1/N \sum_{ij} \frac{V'(r_{ij})}{r_{ij}}$, and $A_3 \approx (d-1)/d$ is of order unity.

Note that δE_3 does not depend on z_1 , so it does not affect the energy minimization with respect to z_1 or z_1 itself. In order to compute z_1 , we thus compute the total energy cost in absence of stress:

$$\delta E^{(0)} = 0.018 k_1 (z_1 - z_c)^2 + \frac{1}{Nd} \sum_{ij}^w V''(r_{ij}), \quad (5)$$

where $k_1 = \langle V'' \rangle_1$ is the average over the $z_1 N/2$ contacts with the highest values of V'' , and \sum_{ij}^w sums over the pairs of particles connected by the $(z - z_1)N/2$ contacts with the smallest values of V'' . By minimizing $\delta E^{(0)}$ with respect to z_1 , we obtain an upper bound on the energy and therefore the frequency, $\omega^* = \sqrt{\delta E_{\min}}$, of the lowest-frequency anomalous modes in the unstressed systems.

In Fig. 2, we compare this theoretical prediction for ω^* with the onset of anomalous modes, ω^\dagger , from simulations in the unstressed system (determined by where $D^{(0)}(\omega)$ reaches 0.25 of its maximum value). The agreement is excellent everywhere, with no adjustable parameters.

Our results show that even though a typical repulsive amorphous solid may have a high coordination number and therefore appear to be far from the unjamming transition, most of the contacts are weak. The number of *stiff* contacts is only slightly in excess of the minimum needed for mechanical stability. This is shown in Fig. 2 (solid triangles) for both potentials at all densities studied. Even

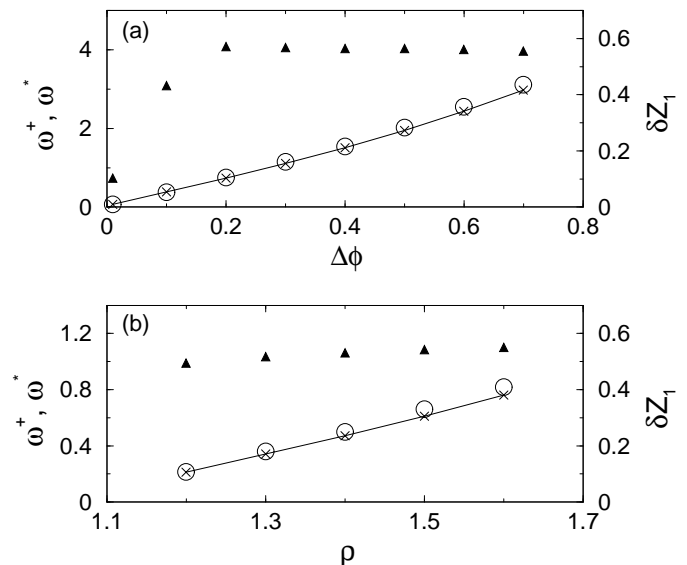


FIG. 2: **Left axis:** The characteristic frequency ω^\dagger (open symbols) calculated from numerical simulations and the corresponding theoretical predictions ω^* (crosses). Lines are to guide the eye and connect the theoretical points. **Right axis:** the fractional deviation from isostaticity $\delta z_1 \equiv (z_1 - z_c)/z_c$ (closed symbols), as functions of (a) distance from the unjamming transition, $\phi - \phi_c$, for repulsive Lennard Jones mixtures and (b) density ρ for Lennard-Jones mixtures.

for the Lennard-Jones system, where the power-law tail of the interaction leads to a divergent total coordination, we find that $(z_1 - z_c)/z_c < 0.6$ at all densities. Thus $(z_1 - z_c)/z_c$ is a small parameter.

While the results of Fig. 2 are for unstressed systems, real glasses have nonzero stresses. To estimate the onset of anomalous modes for systems with stress, we must calculate the total energy cost of a mode, $\delta E = \delta E^{(0)} + \delta E_3$. Fig. 3 shows that for our systems, $\delta E^{(0)} \approx -\delta E_3$, where $\delta E^{(0)}$ is evaluated at its minimum with respect to z_1 for both potentials at different densities. Thus, there is a near cancellation of two large terms leading to a small value of δE (with a large uncertainty) and therefore a very low onset frequency for the anomalous modes in the stressed systems. This is consistent with the finding that the expected scaling of $D(\omega) \sim \omega^2$ for plane-wave normal modes is eclipsed by an approximately linear frequency dependence at small ω for both potentials. The near-cancellation may be a result of the history of how the system was prepared [19].

Our results provide a plausible explanation for the origin of the excess vibrational modes of the boson peak in repulsive glasses. For two commonly-studied models, we have shown that the boson peak derives from the same low-frequency anomalous modes that arise at Point J for systems with finite-ranged repulsions. Several theories have been advanced previously for the boson peak [5, 6, 7, 8, 9, 10, 11, 12]. Fractal systems [5] as well as disordered ones [8, 9, 10] can exhibit excess

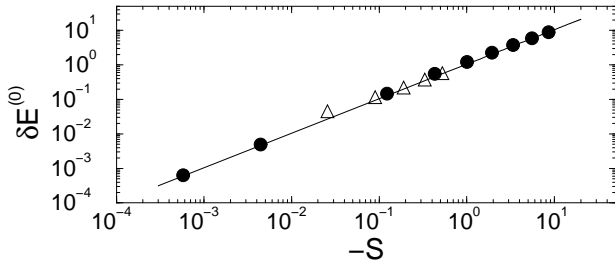


FIG. 3: The energy cost of the lowest frequency anomalous mode for an unstressed system, $\delta E^{(0)}$, as a function of $S \equiv 1/N \sum_{ij} V'(r_{ij})/r_{ij}$ for repulsive Lennard-Jones mixtures (solid circles) and Lennard-Jones mixtures (open triangles). The contribution of the stress term to the energy cost of a mode is $\delta E_3 = A_3 S$, where A_3 is of order unity. The straight line fit corresponds to $\delta E^{(0)} = -1.6S$.

vibrational modes, but glasses are typically not fractal and low-coordination crystals can also display excess modes [16]. Approaches by Phillips [27], Thorpe [28] and Alexander [22] are also based on the idea that a minimum average coordination number is needed to prevent

zero-frequency modes. However, those theories are limited to non-rigid covalent networks or systems interacting with attractive potentials, respectively. By contrast, the approach adopted here from Ref. [20] can be applied to low-coordination crystals, network glasses, as well as repulsive glasses to explain why all these systems exhibit similar structure in the density of vibrational states [20].

For our model glasses, we have shown that $(z_1 - z_c)/z_c$ remains small even when z/z_c is arbitrarily large. It is for this reason that the marginal-coordination approach can be applied to these systems with high coordination. As long as $(z_1 - z_c)/z_c$ is small, the behavior of the glass is governed by the physics of Point J and isostaticity. Even though the unjamming transition itself may be inaccessible—as it is in the Lennard-Jones system studied here—the effect of the longer-ranged part of the potential can be treated as a correction. This theory can therefore be viewed as a conceptual generalization of the perturbation theory of liquids to the case of jamming.

We thank Vincenzo Vitelli for stimulating discussions. This work was supported by DE-FG02-05ER46199 (AJL and NX) and DE-FG02-03ER46088 (SRN and NX).

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